

Charge-Transfer Perturbations of the Electronic Contributions to Electron-Transfer Reactions. Enhanced Donor-Acceptor Couplings Mediated by Coordinated Ligands¹

John F. Endicott* and T. Ramasami

The Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (Received: January 10, 1986; In Final Form: April 1, 1986)

The factors contributing to variations in the adiabaticity of a series of Co(III)-Co(sep)²⁺ (sep = (S)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) cross-reactions have been investigated. Coordinated ligands can be effective in making the electron-transfer rates more adiabatic by altering the electronic structure of the complex and/or by contributing to intermolecular charge-transfer interactions. Alterations of the coordinated ligands change both the ligand field and the charge-transfer excited states of the Co(III) acceptor, and the contributions of each kind of excited state perturbation must be considered in evaluating rate patterns. For Co(NH₃)₅X²⁺ oxidants, the inferred values of the electronic transmission coefficient, κ_{el} , increase systematically through the series X = CN, Cl, Br, N₃, and I with the smallest value of κ_{el} being $\sim 10^{-3}$ and the largest approaching unity. Simple models are proposed which account for the variations in κ_{el} based on the perturbational effects of ligand to metal charge transfer and triplet ligand field excited states on the electron exchange integral coupling reactants and products.

Introduction

The limiting classical description of the rates of electron-transfer processes, as evolved some 25 years ago by Marcus² and by Hush,³ has proved to be very successful.⁴⁻⁷ It is a measure of the importance of this definition of limiting classical behavior in simple electron-transfer reactions that deviations from the classical limit so defined have increasingly been used to explore quantum mechanical effects, nuclear or electronic, on electron-transfer reactivity patterns.^{4,7,8-12}

There has been a resurgence of interest recently in the role of electronic factors in determining the rates of electron-transfer reactions.^{7,8-28} Most of the theoretical and experimental work has been focused on the important questions related to the dependence of electron-transfer rates on the distance of closest approach of the donor and acceptor. Poor spatial overlap of the donor and acceptor orbitals does lead to small values of the electronic matrix element, but other orbital properties (e.g., spin multiplicity changes, changes in orbital occupation, symmetry) can also lead to electronic forbiddenness. Sorting these factors out is complicated by the effects of apparently innocent species in the neighborhood of donor and acceptor which can influence electron-transfer rates by means of their perturbational effects on the electronic coupling between the donor and acceptor centers.

The electronic contributions to electron-transfer reactivity patterns can be most easily visualized in terms of the coupling between donor and acceptor orbitals in the region of their maximum spatial overlap. When the orbital origins (assuming very weak coupling to assure the near independence of donor and acceptor wave functions) are separated by a few atomic diameters, the wave function becomes diffuse in the overlap region, and the donor-acceptor coupling can be appreciably perturbed by environmental species. In principle, these environmental perturbations can be treated by any of several approaches, such as the following: (1) polarization contributions (from environmental species) to the ground-state donor (d) and acceptor (a) wave functions; (2) superexchange contributions to the coupling between donor and acceptor (the perturbation appearing in the usual way as a Hamiltonian operator H' in the matrix element $\langle \psi_d^P \psi_a^R | H' | \psi_d^R \psi_a^P \rangle$ where P and R represent products and reactants and the wave functions are solutions of the zero-order Hamiltonian); (3) var-

(1) Partial support of this research by the National Science Foundation (Grant CHE 80-05497) is gratefully acknowledged.

(2) (a) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. (b) *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (c) *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7.

(3) (a) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 964. (b) *ACS Symp. Ser.* **1982**, *198*, 301.

(4) Ebersson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(5) Bennett, L. E. *Prog. Inorg. Chem.* **1973**, *18*, 1.

(6) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

(7) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, 437.

(8) (a) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 8711. (b) Mok, C.-Y.; Zanella, A. W.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1984**, *23*, 2891.

(9) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *J. Phys. Chem.* **1981**, *85*, 3759.

(10) (a) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431. (b) Endicott, J. F.; Ramasami, T. *J. Am. Chem. Soc.* **1982**, *104*, 5252. (c) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *Ibid.* **1983**, *105*, 5301. (d) Ramasami, T.; Endicott, J. F. *Inorg. Chem.* **1984**, *23*, 3324. (e) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141. (f) Ramasami, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 389.

(11) (a) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537. (b) Nielson, R.; Wherland, S. *Ibid.* **1984**, *23*, 1338.

(12) Taube, H. *Adv. Chem. Ser.* **1977**, *162*, 127.

(13) Chance, B.; DeVault, D. C.; Frauenfelder, H.; Marcus, R. A.; Schrieffer, J. R.; Sutin, N., Eds. *Tunnelling in Biological Systems*; Academic: New York, 1979.

(14) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584. (c) Kuznetsov, A. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 49.

(15) (a) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014. (d) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. (e) Buhks, E.; Jortner, J. *J. Phys. Chem.* **1980**, *84*, 3370. (f) Buhks, E.; Jortner, J. *J. Chem. Phys.* **1981**, *55*, 41. (g) Bixon, M.; Jortner, J. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 17.

(16) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) *Acc. Chem. Res.* **1982**, *15*, 275. (c) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *198*, 105. (d) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(17) (a) Newton, M. D. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 363. (b) *ACS Symp. Ser.* **1982**, *198*, 255. (c) Tembe, B. L.; Friedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982**, *76*, 1490.

(18) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

(19) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7.

(20) Larsson, S. J. *Chem. Soc., Faraday Trans. 2* **1983**, *73*, 1375.

(21) Buhks, E.; Wilkins, R. G.; Isied, S. C.; Endicott, J. F. *ACS Symp. Ser.* **1982**, *198*, 213.

(22) (a) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579. (b) Miller, J. R.; Beitz, J. V. *Ibid.* **1981**, *74*, 6746. (c) Miller, J. R.; Hartman, K. W.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296.

(23) Winkler, J. R.; Nocera, D. G.; Yocum, K. M.; Bordington, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798.

(24) (a) Isied, S. S.; Worsilla, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659. (b) Isied, S. S.; Kuehn, C.; Worsilla, G. *Ibid.* **1984**, *106*, 1722. (c) Isied, S. S.; Vassilian, A. *Ibid.* **1984**, *106*, 1726, 1732.

(25) Chang, A. M.; Austin, R. H. *J. Chem. Phys.* **1982**, *77*, 5272.

(26) Anderes, B.; LaVallee, D. K. *Inorg. Chem.* **1983**, *22*, 2665.

(27) (a) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777. (b) Endicott, J. F.; Tamilarasan, R.; Brubaker, G. B. *J. Am. Chem. Soc.*, in press.

(28) Lee, L. Y. C.; Hurst, J. K., to be published.

iations in the shape of the potential barrier through which the transferred electron is considered to tunnel. While differing somewhat in philosophy and emphasis, the alternative formulations of environmental contributions to the electronic matrix element can be interrelated and should, ultimately, give equivalent results. At the present state of the art, the approach of choice is largely a matter of convenience. In our studies of the perturbational influence of low-energy charge-transfer (CT) excited states on the rates of simple electron-transfer reactions,¹⁰ we have focused largely on the superexchange approach (2). In some recent work^{10f} on the origin of nonadiabatic effects on the rates of certain Co(III)-Co(II) reactions, we have found it convenient to interpret the observations in terms of perturbational corrections to the zero-order wave functions. The present report focuses on the perturbing influence of ligands coordinated to the acceptor and develops an approach to integrating these new observations with those reported earlier.¹⁰

Experimental Section

A. Preparation of Complexes. Literature methods have been used for the synthesis of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (where $\text{X} = \text{CF}_3\text{SO}_3$,²⁹ Cl ,³⁰ Br ,³⁰ I ,³⁰ N_3 ,³¹ and NO_2 ³²), $\text{Co}(\text{Me}_4[14]\text{tetraeneN}_4)(\text{OH}_2)_2^{3+}$,^{33,34} $\text{Co}([14]\text{aneN}_4)(\text{OH}_2)_2^{3+}$,^{33,35} *cis*- $\text{Co}(\text{en})_2\text{ClA}^{36}$ (where $\text{A} = \text{cyclohexylamine (cha)}$, *aniline*, and *benzylamine*) and $\text{Co}(\text{sep})^{3+}$.^{33,37,38} Several other complexes used have been discussed in previous papers in this series.¹⁰ The remaining complexes were synthesized as described below.

$\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ ($\text{X} = \text{CN}$, *cha*, *Aniline*). These complexes were prepared by the reaction of the respective ligands, X , with $\text{Co}(\text{NH}_3)_5\text{O}_3\text{SCF}_3^{2+}$ in predried acetone. Generally a five-to-tenfold excess of the ligands dissolved (or dispersed) in 25–50 mL of dry acetone was added to 1 g of $\text{Co}(\text{NH}_3)_5\text{O}_3\text{SCF}_3^{2+}$, and the mixture was kept in a refrigerator overnight under anhydrous conditions. After rotary evaporation of acetone, the desired crude products were obtained. These were recrystallized from aqueous sodium chloride. The products thus obtained were characterized by means of their elemental analyses and electronic, infrared, and ¹H NMR spectra.

Warning. The perchlorate salts employed in this study are explosive and potentially hazardous.

$[\text{Co}(\text{en})_2(\text{NH}_3\text{cha})\text{Cl}]\text{Cl}_3$. This complex was prepared by the reaction of *cis*- $[\text{Co}(\text{en})_2(\text{cha})\text{Cl}]\text{Cl}_2$ with approximately 1.3 mol of freshly prepared NaNH_2 per mole of Co(III), using either a tetrahydrofuran or dioxan dispersion of the reactants. The reaction proceeded slowly at room temperature and was allowed to run overnight. The solvent was removed by evaporation, and the crude

product was recrystallized as the chloride salt from aqueous hydrochloric acid. The product was yellowish orange and exhibited broad ¹H NMR multiplets at 1.4 ppm for the C_6H_{11} ligand, and complex multiplets at 2.7 ppm for the CH_2 protons of ethylenediamine. The ratio of the integrated multiplets was 1.5:1, compared to the theoretical ratio of 11:8. The electronic spectrum of the recrystallized compound exhibited maxima at 465 and 355 nm, confirming a $\text{Co}(\text{N}_6)$ chromophore. The isomeric composition of this material is not easily determined. Ion exchange chromatography using a Dowex 50W-X2 (200–400 mesh) 15 cm × 0.8 cm column, employing a $\text{HCF}_3\text{SO}_3\text{--NaCF}_3\text{SO}_3$ eluant mixture at 0.5 M ionic strength and $[\text{H}^+] = 0.02$ M revealed two yellowish-orange bands. The minor band, less than 5% of the total Co(III), moved faster and was not identified. The major species (>90%) eluted as a distinct band and had an ¹H NMR spectrum characteristic of *cis*- $\text{Co}(\text{en})_2(\text{cha})\text{X}^{n+}$ complexes.

B. Physical Measurements. Electronic spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra were determined by using KBr pellets in a Perkin-Elmer Model 283 spectrometer. Proton magnetic resonance spectra were determined with either a Varian T-60 or a Nicolet NT-300 spectrometer, samples dissolved in D_2O or CD_3OD , with either Me_4Si or TSP as the internal reference. Electrochemical studies employed a Princeton Applied Research Model 174A polarographic analyzer used in the differential pulse mode, and with platinum, calomel, and hanging mercury drop (or carbon paste) as the counter, reference, and working electrodes, respectively. The differential pulse polarograms were recorded with solutions 0.1 M in NaCF_3SO_3 and at a scan rate of 10 or 20 mV s^{-1} .

C. Kinetic Studies. The rates of reductions of a series of Co(III) complexes by $\text{Co}(\text{sep})^{2+}$, $\text{Ru}(\text{NH}_3)_6^{2+}$, and $\text{Cr}(\text{bpy})_3^{2+}$ were monitored by using stopped flow or spectrophotometric techniques as appropriate. Reactions were run at 25 °C in 0.20 M NaCF_3SO_3 employing pseudo-first-order conditions. Reactant concentrations were chosen so as to avoid potential complications from $\text{Cr}(\text{bpy})_3^{2+}$ or $\text{Co}(\text{sep})^{2+}$ decomposition in acidic solutions.^{37c,39} For the reactions with $\text{Cr}(\text{bpy})_3^{2+}$, $[\text{Co(III)}] \gg [\text{Cr}(\text{bpy})_3^{2+}]$. The $\text{Cr}(\text{bpy})_3^{2+}$ complex was generated in situ by mixing a solution containing the Co(III) oxidant and $\text{Cr}(\text{bpy})_3^{3+}$ with a solution of $\text{Co}(\text{sep})^{2+}$ in the Aminco stopped flow system. Concentrations were selected such that the $\text{Cr}(\text{bpy})_3^{3+}\text{--Co}(\text{sep})^{2+}$ reactions were complete in less than 5 ms, but the Co(III)- $\text{Co}(\text{sep})^{2+}$ reactions would have a lifetime of more than 50 ms. The reactions of $\text{Cr}(\text{bpy})_3^{2+}$ were monitored at 560 nm where this reductant has a molar absorptivity estimated to be $4500 \text{ M}^{-1} \text{ cm}^{-1}$.^{39,40} Pseudo-first-order kinetic plots were linear for 2.5–4 half-lives. Typical concentrations of reagents used were as follows: $[\text{Cr}(\text{bpy})_3^{3+}] = (4\text{--}6) \times 10^{-3} \text{ M}$; $[\text{Co}(\text{sep})^{2+}] = (0.2\text{--}1.0) \times 10^{-4} \text{ M}$; $[\text{Co(III)}] = (2\text{--}200) \times 10^{-4} \text{ M}$; $[\text{H}^+] = (0.1\text{--}1.0) \times 10^{-4}$; $[\text{NaCF}_3\text{SO}_3] = 0.20 \text{ M}$. In some reference reactions it was found that excess free bpy did not affect the observed rates.

D. Evaluation of Apparent Adiabatic Rate Ratios, R_{ad} , and Electron-Transfer Retardation Factors, β_{ab} . The points developed in this report depend on the evaluation of variations in adiabaticity of a closely related series of Co(III)- $\text{Co}(\text{sep})^{2+}$ probe reactions. To accomplish this we have used the corresponding Co(III)- $\text{Ru}(\text{NH}_3)_6^{2+}$ and/or Co(III)- $\text{Cr}(\text{bpy})_3^{2+}$ reactions as relatively adiabatic reference reactions. Details of our procedure are presented elsewhere^{10f} and will be briefly summarized here.

In the classical, adiabatic limit, the rate constant for a cross-reaction can be represented in terms of rate and equilibrium parameters of the component self-exchange reactions by using the Marcus square-root relation^{2-7,16a}

$$k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2} \quad (1)$$

where the k_{ij} are self-exchange rate constants, K_{ab} is the equilibrium constant to the cross-reaction, $\log f_{ab} = (\log K_{ab})^2/4 \log (k_{aa}k_{bb}/A_{aa}A_{bb})$, and the A_{ij} are preexponential coefficients of the

(29) (a) Dixon, N. E.; Jackson, W. G.; Lancaster, M. A.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470. (b) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Ibid.* **1983**, *22*, 846.

(30) Schlessinger, G. G. *Inorg. Synth.* **1967**, *9*, 160.

(31) (a) Linhard, M.; Flygare, H. Z. *Anorg. Allg. Chem.* **1950**, *267*, 328.

(b) Linhard, M.; Wiegel, M. *Ibid.* **1951**, *267*, 121.

(32) Basolo, F.; Murman, R. K. *Inorg. Synth.* **1953**, *4*, 174.

(33) Abbreviations: $\text{bzo}_3[12]\text{hexaeneN}_3 = 3,4:7,8:11,12\text{-tribenzo-1,3,9-triazadodeca-1,3,5,7,9,11-hexaene}$; $\text{sep} = (S)\text{-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane}$; $[14]\text{aneN}_4 = 1,4,8,11\text{-tetraazacyclotetradecane}$; $\text{Me}_2\text{pyro}[14]\text{trieneN}_4 = 2,12\text{-dimethyl-3,7,11,17-tetraazabicyclo[11.3]septadeca-1(17),2,11,13,15-pentaene}$; $\text{Me}_2[14]4,7\text{-dieneN}_4\text{-6-one} = 5,7\text{-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-dien-6-one}$; $2,3,9,10\text{-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene}$; $\text{Me}_6[14]-4,11\text{-dieneN}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$.

(34) Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 394.

(35) (a) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1966**, *5*, 1574.

(b) Poon, C. K.; Mak, P. W. *J. Chem. Soc., Dalton Trans.* **1978**, 216.

(36) (a) Patel, R. C.; Endicott, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 6364.

(b) Bailar, J. C.; Clapp, L. B. *Ibid.* **1942**, *64*, 165. (c) Chan, S.; Leh, F. J. *Chem. Soc.* **1966**, 760.

(37) (a) Creaser, I. I.; Harrowfield, J. MacB.; Herit, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23. (c) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herit, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(38) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(39) (a) Nakano, K.; Narusaura, Y.; Tsuchiya, M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3011. (b) Narusaura, Y.; Nakano, K. *Ibid.* **1980**, *42*, 875.

(40) Ferraudi, G. J.; Endicott, J. F. *Inorg. Chim. Acta* **1979**, *37*, 219.

respective self-exchange rate constants.^{16a} There is evolving evidence that self-exchange reactions tend to be relatively adiabatic,^{8b,10} so eq 1 can be taken as the basis for estimation of relatively adiabatic cross-reaction rate constants. Unfortunately, the pertinent self-exchange and equilibrium parameters are not known for most of the Co(III) oxidants which we have employed. Therefore, it is generally difficult to use eq 1 to analyze the deviations from limiting classical behavior. However, rate ratios may be used advantageously for those systems for which accurate estimates of equilibrium and/or self-exchange parameters are not available. For reactions of a common oxidant ("a") with reductants "b" and "c" we can consider the limiting classical rate ratio

$$R(b:c) = k_{ab}/k_{ac} = \alpha_{cb}(f_{ab}/f_{ac})^{1/2} \quad (2)$$

where, based on eq 1, α_{cb} is independent of the oxidant; i.e., $\alpha_{cb} = (k_{bb}K_{bc}/k_{cc})^{1/2}$ where k_{ab} and k_{ac} are the bimolecular rate constants for the reactions of a with b and c, respectively. In order that we may evaluate deviations in $R(b:c)$ from values based on limiting classical models, the relatively small second-order contributions of the oxidant to $R(b:c)$, through $(f_{ab}/f_{ac})^{1/2}$, must be eliminated. This may be accomplished with respect to an additional reference reaction (reductant d), which permits us to either (a) extrapolate $R(b:c)$ to $(f_{ab}/f_{ac})^{1/2} = 1$ or (b) correct for the numerical value of $(f_{ab}/f_{ac})^{1/2}$. Either approach permits the estimation of a relatively adiabatic or classical rate ratio, $R_{cl}(b:c)$, and calculation of a retardation factor, $\beta_{ab} = R_{obsd}(b:c)/R_{cl}(b:c)$. In practice, since $(f_{ab}/f_{ac})^{1/2}$ is sensitive to variations in the potential of the oxidant (E_a^o), but relatively insensitive to the oxidant self-exchange rate (k_{aa}), we have used the ratio $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$ to define theoretical variations in $(f_{ab}/f_{ac})^{1/2}$ as a function of E_a^o for various values of k_{aa} . Comparison of the theoretical curves, based on eq 1, with the experimental values of $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$ for a given oxidant gives a measure of E_a^o for the oxidant.^{10f} Thus, values of E_a^o , inferred from $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$, can be used parametrically to estimate $R_{cl}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$ for each oxidant. Electrochemical potentials and electron-transfer rate constants for key couples have been experimentally determined in the same media. These measurements have been reported elsewhere.^{10f}

Where potentials are known, or estimated, for the Co(III) oxidants, we estimated $R_{cl}(b:c)$ based on eq 1 and a self-exchange rate, $k_{aa} \sim 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, for the oxidant couple. In order to estimate potentials for $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ couples, we used $E^o \sim 0.47 \text{ V}$ for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ based on $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$, as described above, and the variations in potential found with different axial ligand substitution in $\text{Co}(\text{N}_4)\text{X}_2$ complexes,⁴¹ where N_4 is a tetraaza macrocyclic ligand.

Results

The visible-ultraviolet absorption features used to characterize the complexes synthesized are summarized in Table I.

The rate constants for electron transfer are summarized in Table II. The Co(III)-Cr(bpy)₃²⁺ reactions were well-behaved: the pseudo-first-order plots were linear for at least 3 half-lives and there was no evidence for complications from side reactions. However, the competition technique did limit such studies to some of the slower reactions.

The determination of potentials for the reversible and quasi-reversible couples was usually straightforward and details for most of these systems are given elsewhere.^{10,41} Table II also includes the values of $R_{cl}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$ and β_{ab} inferred for several related Co(III) oxidants.

Discussion

The observed rate ratios, $R_{obsd}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$, are listed in Table II for a large number of Co(III) oxidants and vary by more than a factor of 10³. Rate ratios calculated by using eq 1 predict a much smaller variation for $R_{cl}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$

than observed for the whole range of oxidants considered in this study. The smaller values found for $R_{obsd}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$ than calculated for the adiabatic (i.e., determined by Franck-Condon factors only) rate ratios, $R_{cl}(\text{Co}(\text{sep})^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$, can be attributed to the more appreciable contributions of electronic factors in Co(III)-Co(sep)²⁺ reactions than in Co(III)-Ru(NH₃)₆²⁺ reactions.

Semiclassical Formalisms for Interpreting Electronic Factors. In a semiclassical formulation, the electron-transfer rate constant is given by¹⁶⁻¹⁸

$$k = K_o \kappa_{el} \nu_{eff} \Gamma \exp(-\Delta G^* / RT) \quad (3)$$

where K_o is an outer-sphere (or "ion pair") association constant, κ_{el} is the electronic transmission coefficient, ν_{eff} is the effective nuclear frequency, Γ is the nuclear tunneling correction term, and ΔG^* is the activation energy based on nuclear reorganization and the reactant-product energy gap. The transmission coefficient can be expressed¹⁶⁻¹⁸

$$\kappa_{el} = 2(1 - \exp(-\nu_{el}/2\nu_{eff})) / (2 - \exp(-\nu_{el}/2\nu_{eff}))$$

where ν_{el} is the effective electronic frequency and is proportional to the square of the electronic matrix element, H_{PR} . When $\nu_{el} \ll 2\nu_{eff}$ (small H_{PR})⁷

$$\nu_{eff} \kappa_{el} \approx \frac{2H_{PR}^2}{h} \left(\frac{2\pi^3}{2E_{out}RT + E_{in}h\nu_{in} \cosh(h\nu_{in}/2k_B T)} \right)^{1/2} \quad (4)$$

in which E_{in} and E_{out} are reorganizational energies for the first coordination sphere and the solvent, respectively, and $h\nu_{in}$ is the mean vibrational quantum associated with E_{in} . Since ν_{in} is a much higher frequency vibration than ν_{out} , solvent reorganization may be treated as a preequilibrium in our systems, so, $\nu_{eff} \approx K_{out}\nu_{in}$.⁷ For a representative set of parameters ($h\nu_{in} \approx 400 \text{ cm}^{-1}$, $\nu_{eff} \sim 8 \times 10^{13} \text{ s}^{-1}$, $E_{in} \sim 10 \times 10^3 \text{ cm}^{-1}$, $E_{out} \sim 2 \times 10^3 \text{ cm}^{-1}$, $K_o \sim 10^{-3}$), and $\kappa_{el} \sim H_{PR}^2 \times (10^5 \text{ eV}^{-2})$.

Theoretical considerations^{7,13-15} and experimental observations^{10,11,22-24,26-28} indicate that H_{PR} decreases rapidly with donor-acceptor separation, r_{DA} . A simple exponential dependence^{7,10,22-28,42}

$$H_{PR} \approx H_{PR}^0 \exp(-\alpha r_{DA}) \quad (5)$$

is commonly used, where α can be interpreted as an orbital parameter characteristic of the donor and acceptor systems. For purposes of our discussion it is convenient to interpret H_{PR} as a quasi-bonding interaction between the donor and acceptor, with the exponential term in (5) being interpreted as an overlap integral between spherical donor and acceptor wave functions.⁴² This view will be developed further below. At this point we note that evaluation of H_{PR} requires a knowledge of the donor and acceptor wave functions in the region far from the nuclei of origin. If a spherical wave approximation is used for the wave functions in this region, as in eq 5, then one must anticipate that H_{PR}^0 and/or α may have to be adjusted to compensate for inadequacies in this approximation. If the spherical wave approximation is a reasonable initial approximation, then the corrections can be treated as perturbations. The net effect of such perturbations can, in principle, lead to relatively large values of H_{PR} even for r_{DA} reasonably large. Among the electronic perturbations which are most likely to be important are those which mix low-energy electronic excited states with the zero-order wave functions. Thus, we have been able to demonstrate a systematic increase in simple electron-transfer rates which can be attributed to the decreasing energies of ion-pair charge-transfer excited states.¹⁰ The more complex effects of coordinated ligands, through the variations in energies of metal-to-ligand charge-transfer (MLCT) states, are considered in this report.

Evaluation of Rate Variations Ascribable to Ligand-to-Metal Charge-Transfer States in the Oxidant. We have employed a simple series of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ complexes to investigate the effects of coordinated ligand-to-metal CT states on electron-transfer rates.

(41) Rillema, D. P.; Endicott, J. F.; J. F.; Papaconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

(42) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

TABLE I: Visible Spectral Details of Co(III) Ammine Compounds^a

compd	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)		
	¹ A ₁ → ¹ T ₁	¹ A ₁ → ¹ T ₂	¹ A ₁ → ¹ T ₂
Co(NH ₃) ₅ cha ³⁺	478 (62)		340 (55)
Co(NH ₃) ₅ CN ²⁺	440 (56)		326 (55)
Co(NH ₃) ₅ amline ³⁺	480 (66)		345 (65)
Co(NH ₃) ₅ (en) ₂ cha ³⁺	460 (76)		352 (70)
Co(NH ₃) ₆ ³⁺	475		339
Co(en) ₃ ³⁺	466		339

^a 0.20 M NaCF₃SO₃, [H⁺] = 10⁻³ M.

TABLE II: Kinetic Parameters

oxidant (a)	k_{obs} , M ⁻¹ s ⁻¹		$R(\text{Co(III)}-\text{Ru(II)})$		β_{R^f}	E_{R^f} , V	$E_{\text{max}}(\text{CT})$, kJ mol ⁻¹
	Co(sep) ²⁺ (b)	Ru(NH ₃) ₆ ²⁺	obsd	adiab			
Co(NH ₃) ₆ ³⁺	0.15 ± 0.01 (9)	0.006 ^f	25	39 ^g	0.6	-0.06	500
Co(NH ₃) ₅ cha ³⁺	0.14 ± 0.01 (5)	0.07 ± 0.001 (5)	2	26 ^g	0.1	+0.085	
Co(NH ₃) ₅ amline ³⁺	0.60 ± 0.05 (5)	0.11 ± 0.01 (5)	5.5				
Co(NH ₃) ₅ CN ²⁺	0.58 ± 0.03 (5)	4.6 ± 0.2 (5)	0.12	52 ^g	0.003	-0.17	438
Co(NH ₃) ₅ Cl ²⁺	58 ± 4 (6)	260 ^h	0.22	12 ^g	0.02	+0.5	383
Co(NH ₃) ₅ Br ²⁺	(1.6 ± 0.1) × 10 ³ (5)	1.6 × 10 ^{3h}	1	11 ^l	0.09	+0.6 ^l	310
Co(NH ₃) ₅ I ²⁺	(1.2 ± 0.1) × 10 ⁴ (4)	6.7 × 10 ^{3h}	1.8	7 ^l	0.26	0.75 ^l	300
Co(NH ₃) ₅ N ₃ ²⁺	7.4 ± 0.5 (4)	1.2 ^h	3.6	19 ^l	0.2	+0.24 ^l	363
Co(NH ₃) ₅ NO ₂ ²⁺	(2.1 ± 0.15) × 10 ³ (5)	80 ± 5 (4)	26 ^l	~19	~1	+0.3 ^l	
cis-Co(en) ₂ (cha)Cl ²⁺	0.82 ± 0.06 (6)	45 ^k	0.018	13 ^g	0.001	+0.45	
cis-Co(en) ₂ (amline)Cl ²⁺	3.3 ± 0.25 (4)	56 ^k	0.056	12 ^l	0.005	+0.55 ^l	
cis-Co(en) ₂ (benzylamine)Cl ²⁺	85 ± 6 (4)	37 ^k	2.3	19 ^l	0.1	+0.25 ^l	
cis-Co(en) ₂ (CN)Cl ²⁺	1.2 ± 0.05 (5)	0.10 ± 0.01 (4)	12	32 ^l	0.4	+0.005	
Co(phen) ₃ ³⁺	24 ± 1 (4)	11.4 ± 0.8 (4)	2.2	48 ^m	0.046	-0.12 ^m	
Co([14]aneN ₄)(NH ₃) ₂ ³⁺	(4.8 ± 0.4) × 10 ³ (6)	(9.3 ± 0.8) × 10 ³ (6)	0.51	11 ^m	0.046	+0.38 ^m	
Co([14]aneN ₄)(OH) ₂ ³⁺	0.10 ± 0.01 (5)	(4.5 ± 0.3) × 10 ⁻² (4)	2.3	44 ^g	0.04	+0.18	
Co(Me ₄ [14]tetraeneN ₄)(NH ₃) ₂ ³⁺	36 ± 6 (5)	1.1 ± 0.1 (4)	27	28 ⁿ	0.97	0.00 ⁿ	
Co([14]aneN ₄)(OH) ₂ ³⁺	(1.6 ± 0.4) × 10 ³ (4)	(1.0 × 0.1) × 10 ³ (4)	1.6	10 ^o	0.16	0.421 ^o	
Co(Me ₄ [14]tetraeneN ₄)(OH) ₂ ³⁺	(1.7 ± 0.1) × 10 ⁴ (4)	(1.10 ± 0.05) × 10 ⁵ (4)	1.7	5 ^o	0.34	7.564 ^o	
meso-Co(bzo) ₂ [12]hexaeneN ₂ ³⁺	100 ± 7 (5)	55 ± 6 (4)	1.8	26 ^m	0.07	0.06 ^m	
rac-Co(bzo) ₂ [12]hexaeneN ₂ ³⁺	780 ± 60 (4)	(1.4 ± 0.1) × 10 ³ (4)	0.56	26 ^m	0.02	0.06 ^m	

^a 25 °C, 0.1 M ionic strength except as indicated. ^b $R' = R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$. ^c $\beta_{\text{R}^f} = R(\text{obsd})/R(\text{adiabatic})$ for therations of rate constants from Co(III)-Co(sep)²⁺ and Co(III)-Ru(NH₃)₆²⁺ reactions. ^d Inferred from eq 1 and $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$; see note g. ^e Reference 47 except as indicated. ^f Taube, H.; Geselowitz, D. *Adv. Inorg. Bioinorg. Mechanisms* 1982, 1, 391. ^g Based on E^f as inferred from eq 1 and $R(\text{Cr}(\text{bpy})_3^{2+}:\text{Ru}(\text{NH}_3)_6^{2+})$; the self-exchange rate constant, k_{e} , was taken to be 10⁻⁴ M⁻¹ s⁻¹ for Co(III) oxidants except for a value of 10⁻⁶ M⁻¹ s⁻¹ used for Co(NH₃)₆³⁺. ^h Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* 1964, 86, 1686. ⁱ Candlin, J. P.; Halpern, J.; Trimm, D. L. *J. Am. Chem. Soc.* 1964, 86, 1019. ^j Estimate of E^f based on value for Co(NH₃)₅Cl²⁺ and variations of potential with axial ligands as in ref 41. Other parameters as in note e. ^k Patel, R. C.; Endicott, J. F. *J. Am. Chem. Soc.* 1969, 90, 6364. ^l Estimate of E^f based on value for Co(en)₂(cha)Cl²⁺, as in note g, and ascribing the variations in notes of Co(III)-Ru(NH₃)₆²⁺ reactions to variations in equilibrium constants when eq 1 is used. Other parameters as in note g. ^m E^f determined from differential pulse voltammetry, quasi-reversible wave. ⁿ E^f as reported in: Rillema, D. P.; Endicott, J. F. *Inorg. Chem.* 1973, 12, 1712. ^o E^f as reported in Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* 1979, 101, 1131. Self-exchange parameters as reported in: Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmoueses, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* 1981, 103, 1431.

We find that β_{ab} increases, in a reasonably systematic way, with decreasing energy of the lowest energy MLCT absorption band of the acceptor (Table II).

The effect of the CT perturbations on the reactant-product coupling, or H_{PR} , depends on the vertical transition-state-charge-transfer excited-state energy gap, E_{CT}^* . This can be represented as^{10b}

$$E_{CT}^* = E_{CT}^{\circ} - \Delta G^* - \delta \quad (6)$$

where δ is the difference in energy of the CT excited state when it has the nuclear coordinates of the ground state and when it has the nuclear coordinates of the electron-transfer transition state, and E_{CT}° is the vertical CT transition energy from the reactants. Estimates of δ may be obtained assuming that the potential energy varies as the square of the displacements of the nuclear coordinates; thus^{8b}

$$\delta \approx -(f_{CT}/f_R)\{\Delta G^* - 2[\Delta G^*(E_{CT}^* - E_{CT}^{\circ})/f_{CT}]\}^{1/2} \quad (7)$$

where f_{CT} and f_R are mean force constants for the appropriate vibrations of the CT excited-state and the ground-state reactants, respectively, and E_{CT}° is the energy of the CT excited state with the appropriate equilibrium nuclear coordinates. The quantity $(E_{CT}^* - E_{CT}^{\circ})$ is related to the band shape of the $R \rightarrow CT$ absorption and can be approximated by the full width at half-height ($\Delta\omega_{1/2}$) of this absorption;^{43,44} however, f_{CT} is usually an unknown quantity. A somewhat simpler expression can be obtained by assuming that the equilibrated CT excited state and the products have similar nuclear coordinates^{10b,45}

$$\delta \approx -[(f_R/f_P)(\Delta G^*/\lambda) - 2(f_R\Delta G^*/f_P\lambda)^{1/2}](E_{CT}^* - E_{CT}^{\circ})$$

where f_P is the mean force constant for the appropriate product vibrations and λ is the Marcus reorganizational parameter² ($\lambda = 4[E_{in} + E_{out}]$). If one makes the usual assumption that the reactant and product force constants are approximately equal (i.e., that $f_R \approx f_P$), one can use $\Delta G^* = (\lambda/4)(1 - \Delta G^{\circ}/\lambda)^2$ (where ΔG° is the free energy change for the $R \rightarrow P$ reaction) to further obtain

$$\delta \approx [1 - (1/4)(1 + \Delta G^{\circ}/\lambda)^2](E_{CT}^* - E_{CT}^{\circ}) \quad (8)$$

Fortunately, δ is usually less than 25% of E_{CT}^* and eq 7⁴⁶ and 8 give results that agree within the uncertainties of the estimates used. The values of E_{CT}^* used in Figure 1 have been estimated by using eq 6 and 8. For these values of E_{CT}^* we have used experimental LMCT absorption maxima for E_{CT}^* , experimental estimates of E_{CT}° ,⁴⁷ and $\lambda \sim 290$ kJ mol⁻¹.⁴⁸

Evaluation of the Electronic Mismatch for Co(III)-Co(II) Reaction Systems. Our earlier study of ion-pair charge-transfer perturbations of electron-transfer rates^{10b} employed a set of re-

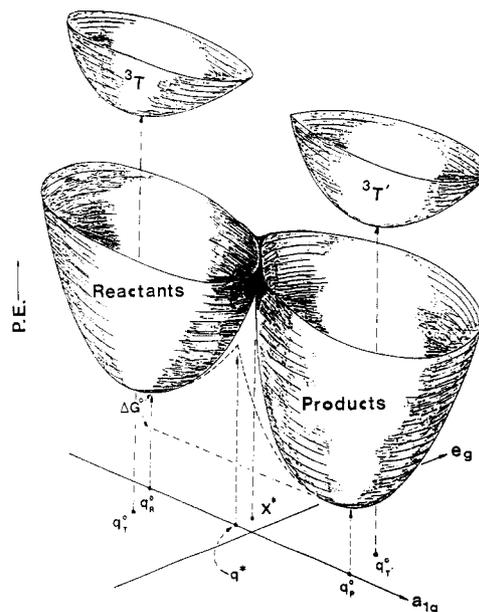


Figure 1. Qualitative representation of potential energy surfaces of an electron-transfer reaction perturbed by low-energy ligand field excited states. Surfaces are based on $\text{Co}(\text{NH}_3)_6^{3+,2+}$ and $\text{Co}(\text{sep})^{3+,2+}$. Only a single excited state is included, triplet Co(III), for the reactants and products. These excited states are considered to be distorted mostly along a coordinate, constructed from molecular e_g normal modes, which is orthogonal to the normal reaction coordinate and slightly distorted along the reaction coordinate constructed from molecular a_{1g} normal modes (parallel to the normal reaction coordinate). Each surface represents a Co(III) and Co(II) pair; Co(II) contributions to the excited-state surfaces have not been explicitly considered.

actions in which the electronic structures of the reactant pair ($\text{Co}(\text{phen})_3^{3+}$ and $\text{Co}(\text{sep})^{2+}$) was nearly constant. However, the variations in LMCT energies necessarily result in changes in the energies of low-energy, metal-centered (LF) electronic states as well. We have shown elsewhere that variations in the energies of these LF states can result in the electronic retardation of the resulting electron-transfer rates.^{10f} The relationship of this retardation of electron-transfer rates to the CT enhancement of rates must be examined before we can proceed further.

A major component of the electronic retardation of Co(III)-Co(II) cross electron-transfer reaction rates appears to have its origin in the difference in energies of triplet Co(III) (reactant and product) and probably doublet Co(II) (reactant and product) LF electronic excited states.^{10f} These LF excited-state contributions to the reaction rates probably arise because contributions of the excited-state electronic configurations are necessary to permit the otherwise forbidden Co(III)/Co(II)⁴⁹ electron transfer. The influence of these LF excited states can be treated in terms of perturbational contributions to the ground-state wave function, and the experimental observations indicate that the electronic retardation factor (β_{el}) is related to the difference in reactant and product excited-state energies (ΔE_{ex}) by^{10f}

$$RT \ln \beta_{el} \approx 0.5[\Delta E_{ex}] + b \quad (9)$$

where b is approximately constant. This behavior can be described in terms of a relatively simple perturbation theory model, or possibly by the direct population of Co(II) excited states.⁵⁰

The condition for electron transfer can be expressed in terms of the set of configuration coordinates (q_i^*) which result in the smallest energy for which the total wave functions of the reactants (Co(III) and Co(II)) and the products (Co(II) and Co(III)) are equal. Using the Born-Oppenheimer approximation, this condition

(43) For a Gaussian absorption band with a threshold energy, E_{CT}° , occurring where the peak intensity falls to about 5%,⁴⁴ $E_{CT}^* - E_{CT}^{\circ} \approx \Delta\omega_{1/2}$.

(44) Fleischauer, P. D.; Adamson, A. W.; Sartori, G. *Prog. Inorg. Chem.* **1972**, *17*, 1.

(45) This is equivalent assuming that the effective nuclear displacements are approximately the same for the various ground-state Co(III)-Co(II) couples, as for the difference in nuclear coordinates between the ground-state $\text{Co}^{\text{III}}(\text{NH}_3)_6(\text{X}^-)$ species and the vibrationally equilibrated charge transfer excited state, $[\text{Co}^{\text{II}}(\text{NH}_3)_6(\cdot\text{X})]$ (see Figure 3 in ref 10c). The ground-state Co(II) species considered here all have high-spin (quartet) electronic configurations while the electronically correlated $[\text{Co}^{\text{II}}(\text{NH}_3)_6(\cdot\text{X})]$ species would be a low-spin (doublet) species. However, it has been inferred that there is considerable mixing of these spin states along this excited-state nuclear distortion coordinate (Endicott, J. F.; Ferraudi, G. J. *Inorg. Chem.* **1975**, *14*, 3133), and the equilibrated species probably differs little from the quartet.

(46) Our estimates of δ using eq 7 employed $f_{CT}/f_R \sim 0.5$: f_R represents an average of the force constants for nearly symmetrical nuclear motions (a_{1g} in O_h symmetry) of the ground-state Co(III) and Co(II) complexes, while f_{CT} must represent mostly the "symmetric stretch" (e_g in O_h symmetry) of a Co(II) species, along a coordinate leading to a tetragonally distorted (D_{4h}) electronic excited state.

(47) (a) Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630. (b) Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 494.

(48) For the $\text{Co}(\text{sep})^{3+,2+}$ couple, $\lambda \approx 240$ kJ mol⁻¹³⁷ and values of λ for the cobalt ammine complexes are usually 300-400 kJ mol⁻¹.^{10c} Thus the cross-reactions will have values $\lambda \sim 290 \pm 30$ kJ mol⁻¹.

(49) While it is commonplace to refer to these reactions as "spin forbidden", there need be no spin constraint, as such, on the nonradiative process in a collision complex; i.e., spin is conserved in the process ${}^4\{({}^1A_1\text{Co}(\text{III}), ({}^4T_1)\text{Co}(\text{II})\} \rightarrow {}^4\{({}^4T_1)\text{Co}(\text{II}), ({}^1A_1)\text{Co}(\text{III})\}$. The forbiddenness originates from the three-electron nature of this transition.

(50) This argument was suggested to us by Professor M. C. Zerner.

can be reexpressed in terms of separate equality of the respective electronic and nuclear wave functions.^{10f} One generally constructs a minimum reaction trajectory which involves displacement only of those nuclear coordinates which are different in the equilibrium geometries of the reactants and products. The maximum along this trajectory corresponds to some specific set of values (q^*) for the distortion coordinates. Configuration coordinates not implicated in the minimum reaction trajectory can assume any value and the condition for equality of the nuclear wave functions can still be met, but the condition for equality of the electronic wave functions need not be met for all these values of the remaining coordinates.

For simplicity of the discussion we will focus our attention on the electronic wave functions of the Co(III) reactant and product species (an alternative, which emphasizes Co(II) reactant and product excited states, is presented below). We need to find a set of nuclear coordinates for which

$$\psi_{\text{Co(III)}}^{\text{P}}(r; q) = \psi_{\text{Co(III)}}^{\text{R}}(r; q)$$

(r and q being the electronic and nuclear coordinates, respectively; for simplicity, and because $E(^2\text{E})$ varies little for the Co(II) complexes, it is assumed that $\psi_{\text{Co(II)}}^{\text{Z}} \sim \text{constant}$). These wave functions for the ground electronic state may be expressed in the form

$$\psi_{\text{Co(III)}}^{\text{Z}}(r; q) = {}^1\psi_{\text{Co(III)}}^{\text{Z}}(r; q) + \gamma {}^3\psi_{\text{Co(III)}}^{\text{Z}}(r; q)$$

where ${}^1\psi_{\text{Co(III)}}^{\text{Z}}(r; q)$ and ${}^3\psi_{\text{Co(III)}}^{\text{Z}}(r; q)$ are the zero-order singlet- and triplet-state wave functions, respectively, and γ is a spin-orbit mixing coefficient which increases in value as the ground-state-triplet LF excited-state energy gap decreases. One expects the triplet states of Co(III) to be distorted along a nuclear coordinate different from that involved in the electron-transfer reaction. For example, the reaction trajectory for electron transfer in the Co(NH₃)₆^{3+,2+} couple is constructed from contributions of the totally symmetric molecular a_{1g} vibrational modes, while the lowest energy triplet state of Co(NH₃)₆³⁺ is distorted in an orthogonal e_g mode⁵¹ (see Figure 1). As a consequence, some nuclear coordinate X can be found, which is different from the nuclear coordinate of the minimum displacement reaction trajectory, such that distortion in X will increase the energy gap to the reactant Co(III) triplet state (E_{T}^{R}) and decrease the energy to the product Co(III) triplet state (E_{T}^{P}), or vice versa. The system, distorted by an amount X^* , will be altered in energy by an amount $\epsilon(X^*)$ such that

$$E_{\text{T}}^{\text{P}}(X^*) - \epsilon(X^*) = E_{\text{T}}^{\text{R}}(X^*) + \epsilon(X^*)$$

The additional energy required for this distortion is therefore

$$\epsilon(X^*) = |\Delta E_{\text{T}}|/2$$

This analysis suggests a model for these systems in which there are two relaxation pathways in the neighborhood of the saddle point of the usual reaction trajectory: (a) an electronically forbidden passage to products when the coordinate which satisfies the condition for equality of the nuclear wave functions is distorted to have the value of q^* ; (b) an electronically allowed passage to products for distortion of an additional nuclear coordinate to a value X^* which results in equality of the electronic as well as the nuclear wave functions. This suggests that the net electronic retardation can be represented

$$\beta_{\text{RP}} \approx \beta_{\text{RP}}' + \eta K(X) = \beta_{\text{RP}}' + \eta \exp(-|\Delta E_{\text{T}}|/2RT) \quad (10)$$

where η allows for less than equal weighting of the contribution from triplet terms. Equation 10 nicely accounts for our previously reported dependence of the retardation factors on variations in the difference of reactant and product triplet-state energies. In this model, the two relaxation pathways are competitive and electronic perturbations can only affect the electronically forbidden pathway (β_{RP}). Equation 10 provides us with a means for evaluating these perturbations. Of the pentaammine complexes considered here, Co(NH₃)₅CN²⁺ and Co(NH₃)₅Cl²⁺ appear to

only reflect contributions of the triplet terms^{10f} and this suggests a value of $\eta \sim 0.4$.

The doublet excited states of the Co(II) ammine complexes lie at relatively low energies (the vibrationally equilibrated doublets of Co^{II}(NH₃)₅X probably have energies of about $4 \times 10^3 \text{ cm}^{-1}$ greater than their ground states, if one allows for a typical LF band width of about $3 \times 10^3 \text{ cm}^{-1}$).^{10f} These states are low enough in energy that, on many reaction surfaces, the product (²E)Co(II) state must be thermodynamically accessible from the ground-state reactants; e.g., this appears to be the case for Co(NH₃)₅X²⁺-Co(sep)²⁺ reactions when X = Cl, Br, I, or NO₂. Thus these low-lying doublet states must make an appreciable contribution to the interactions along the reaction coordinate. However, one expects the vibrationally equilibrated (²E)Co(II) excited states to be tetragonally distorted, e.g., in a manner similar to the large tetragonal distortions characteristic of low-spin Co(II) complexes containing macrocyclic ligands.⁵² As a consequence, crossing to a (²E)Co(II)-(¹A)Co(III) products surface from any reactant surface is bound to be characterized by very large nuclear reorganizational barriers.^{10e,53} Our very rough estimates would place these (²E)Co(II)-(¹A)Co(III) surfaces at several tens of kilojoules per mole above the energy of the transition state for the apparent adiabatic reactants \rightarrow products crossing (i.e., with coordinates q^* , above). A perturbational treatment of these states would lead to a correlation between retardation factors and energy differences of reactant and product (²E)Co(II) species similar in form to eq 10. Consideration of the lowest energy LF excited states for Co(III) and Co(II) species, for both the reactants and products, will lead to the replacement of $|\Delta E_{\text{T}}|$ in eq 10 by a sum over the triplet and doublet excited state energy differences, as in our original report.^{10f} The generalization of the argument presented above seems straightforward, but it is conceptually complicated. Values of $E(^2\text{E})$ vary much less than the triplet energies of Co(III) in the Co(NH₃)₅X complexes, so the empirical correlation used seems adequate to correct for variations in LF excited-state structure.

An alternative explanation of the dependence of β_{ab} on LF electronic excited states involves promotion of the Co(II) reactant species to the ²E state and reaction with Co(III) to produce Co(III) and (²E)Co(II) products.⁵⁰ From a strictly classical point of view, the ratio of rates for this doublet (D) and the quartet (Q) reaction pathways is given by

$$-RT \ln (k_{\text{D}}/k_{\text{Q}})_{\text{cl}} = E(^2\text{E}^{\text{R}}) + (\lambda_{\text{D}} - \lambda_{\text{Q}})/4 + \Delta E(^2\text{E})/2 + (\Delta G_{\text{D}}^{\circ})^2/\lambda_{\text{D}} - (\Delta G_{\text{Q}}^{\circ})^2/\lambda_{\text{Q}} \quad (11)$$

(where $E(^2\text{E}^{\text{R}})$ is the energy difference between the vibrationally equilibrated doublet and the ground-state Co(II) reactant, $\Delta E(^2\text{E}) = E(^2\text{E}^{\text{P}}) - E(^2\text{E}^{\text{R}})$ and λ_{D} and λ_{Q} are the reorganizational parameters characteristic of the doublet and quartet pathways). Since typical values are $E(^2\text{E}^{\text{R}}) \sim 50 \text{ kJ mol}^{-1}$, $|\Delta E(^2\text{E})| \sim 10 \text{ kJ mol}^{-1}$ and the quadratic terms cannot contribute more than 10 kJ mol^{-1} , this doublet-to-doublet pathway can be kinetically realistic only if $\lambda_{\text{D}} \ll \lambda_{\text{Q}}$. This does not seem consistent with available information about low-spin Co(III)-Co(II) electron-transfer couples;^{10e,53} i.e., for the model systems examined⁵³ $\lambda_{\text{D}} \sim \lambda_{\text{Q}}$. Furthermore, the doublet reaction channel tends to predict the incorrect order of rate ratios (e.g., our approximate energy estimates lead to $R_{\text{cl}}(\text{estd}) \sim 0.15, 0.04,$ and 0.01 for the doublet pathway, compared to $R_{\text{cl}}(\text{obsd}) = 0.12, 0.022,$ and 25 , respectively, for Co(NH₃)₅CN²⁺, Co(NH₃)₅Cl²⁺, and Co(NH₃)₆³⁺ for Co(sep)²⁺ and Ru(NH₃)₆²⁺ reductants), and this reaction channel predicts classical rate constants that are too small (by factors of $10^{4\pm 2}$) even when λ_{D} is assumed equal to the reorganizational parameter (λ_{Ru}) for the Ru(NH₃)₆^{3+,2+} couple. Similarly, we estimate that (⁴T)Co(II) products would be kinetically favored

(52) Endicott, J. F.; Lilie, J.; Kuszaj, J. M.; Ramaswamy, R. S.; Schmonsees, W. G.; Simic, M. G.; Glick, M. D.; Rillema, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429.

(53) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431.

(51) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

over (²E)Co(II) products of Co(III)–Ru(NH₃)₆²⁺ reactions by factors of 10^{3±1}, even if λ_D were as small as λ_{Ru}. Thus, the information currently available to us indicates that direct population of (²E)Co(II) reactant and/or product states cannot account for the observed correlation of inferred retardation factors with variations in reactant and product electronic structure,^{10f} as summarized in eq 9. However, it is clear that the (²E)Co(II) states are low enough in energy that their contribution must be considered on a system by system basis. At the present time, the perturbational argument presented above seems most consistent with information available about the systems (with relatively high-energy CT excited states) on which eq 9 is based.

An Exchange Interaction Model for the CT Perturbations of Electron-Transfer Rates. The mixing of reactant and product wave functions is allowed by the electron exchange operator;⁴² i.e.

$$H_{PR} = \langle \psi_d^P \psi_a^P | H_{\text{exch}} | \psi_d^R \psi_a^R \rangle \\ = \int \psi_{\text{Co(III)}}^P \psi_{\text{Co(III)}}^R (e^2/r) \psi_{\text{Co(II)}}^P \psi_{\text{Co(II)}}^R d\tau$$

For simplicity of this discussion, we consider only the effect of perturbations at the forbidden crossing (i.e., with nuclear coordinates *q*^{*}), so that the triplet components are not explicitly considered, and we consider the Co(II) wave functions to be insensitive to the CT perturbations. We may then write the Co(III) wave functions in the form

$$\psi_{\text{Co(III)}}^z \approx {}^0\phi_{\text{Co(III)}}^z + v^z \phi_{\text{CT}}^z$$

where the CT perturbation results in the second term on the right. Substituting for ($\psi_{\text{Co(III)}}^P \psi_{\text{Co(III)}}^R$), ignoring terms second order in the perturbation, and setting

$$\int {}^0\psi_{\text{Co(III)}}^P {}^0\phi_{\text{Co(III)}}^R (e^2/r) \phi_{\text{Co(II)}}^P \phi_{\text{Co(II)}}^R d\tau \approx 0$$

since the unperturbed transition is forbidden, we obtain

$$H_{PR} \approx \int [{}^0\phi_{\text{Co(III)}}^P v^R \phi_{\text{CT}}^R + v^P \phi_{\text{CT}}^P {}^0\phi_{\text{Co(III)}}^R] (e^2/r) \times \\ [\phi_{\text{Co(II)}}^P \phi_{\text{Co(II)}}^R] d\tau$$

For $v^z \approx a/E_{\text{CT}}^z$ ($Z = R$ or P), and setting

$$\int {}^0\phi_{\text{Co(III)}}^P \phi_{\text{CT}}^R (e^2/r) {}^0\phi_{\text{Co(III)}}^P \phi_{\text{Co(II)}}^R d\tau \approx \\ \int \phi_{\text{CT}}^P {}^0\phi_{\text{Co(III)}}^R (e^2/r) \phi_{\text{Co(II)}}^P \phi_{\text{Co(II)}}^R d\tau \approx b/a$$

we obtain

$$H_{PR} \approx b \left(\frac{1}{E_{\text{CT}}^R} + \frac{1}{E_{\text{CT}}^P} \right) \quad (12)$$

Equations 4, 10, and 11 provide the basis⁵⁴ for correlating the rate retardations observed for the Co(NH₃)₅X²⁺–Co(sep)²⁺ reactions (Figures 2 and S-1,⁵⁵ parameters used in generating these correlations are summarized in Tables II and S-I).⁵⁵

Conclusions

Marcus' classical description of electron-transfer rates has been used as the basis for demonstrating that certain Co(III)–Co(II) electron-transfer reactions have rates which are at least 3 orders

(54) Since the (²E)Co(II) product excited states are probably thermodynamically accessible from many of the (¹A)Co(III)–(⁴T)Co(sep)²⁺ reactants, one must consider the possible involvement of a $\{({}^1\text{A})\text{Co(III)}, ({}^4\text{T})\text{Co(sep)}^{2+}\} \rightarrow \{({}^2\text{E})\text{Co(II)}, ({}^1\text{A})\text{Co(sep)}^{2+}\}$ pathway in these reactions. The kinetic advantage of the pathway (D) leading to (²E)Co(II) products over that (Q) leading to (⁴T)Co(II) products over that (Q) leading to (⁴T)Co(II) products can be expressed

$$\Delta G_D^* - \Delta G_Q^* = (\lambda_D - \lambda_Q)/8 + E({}^2\text{E}^P)/2 + [E({}^2\text{E})]^2/2(\lambda_Q + \lambda_D) + \\ [\Delta G_Q^*]^2/(2(\lambda_Q + \lambda_D) - 1/\lambda_Q)/4 + [\Delta G_Q^*][E({}^2\text{E}^P)]/(\lambda_Q + \lambda_D)$$

As a maximum contribution, for λ_D = λ_{Ru}, we estimate that $k_D \approx k_Q \times 10^{-3\pm 1}$ for all of these systems except the Co(NH₃)₅NO₂²⁺–Co(sep)²⁺ reaction, for which $k_D \sim 0.15k_Q$. This raises the possibility of contributions of a (²E)Co(II) pathway in the system which deviates most from our correlation (Figure 2).

(55) Supplementary information, see paragraph at end of paper.

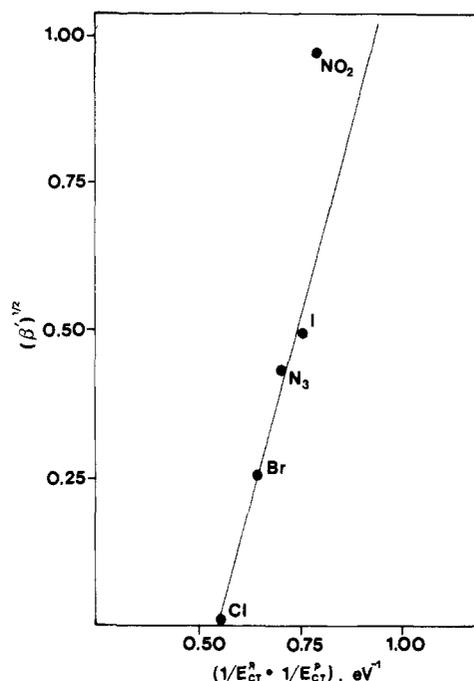


Figure 2. Correlation of the experimental retardation factor, β_{RP} , corrected for variations in triplet-state energies, $(\beta_{\text{RP}})_{\text{cor}} = \beta_{\text{RP}} - 0.4 \exp(-\Delta E_{\text{T}}/2RT)$, with the energies of the lowest energy reactant and product CT excited states.

of magnitude slower than expected on the basis of consideration of nuclear reorganizational parameters. This rate retardation results from an electronically forbidden crossing, and variations in its magnitude can be correlated with the difference in reactant and product electronic structure, more specifically with the sum of the energy differences between Co(III) reactant and product LF triplet excited state energies and the Co(II) reactant and product doublet excited-state energies.

The Co(III)–Co(II) electron-transfer rates approach the predicted classical limit as this energy difference (ΔE_{ex}) approaches zero,^{10f} and the retardation factor is proportional to $\exp(-|\Delta E_{\text{ex}}|/2RT)$. The correlation with ΔE_{ex} can be described by using an exchange coupling model for H_{PR} , by a simple two-channel model for the transition state: (a) an electronically forbidden channel; and (b) an electronically allowed channel generated by spin orbit coupling to LF triplet excited states along distortion coordinates for these excited states.

Examination of the effects of charge-transfer perturbations on the electronically forbidden reaction channel in Co(NH₃)₅X²⁺–Co(II) reactions is complicated by the simultaneous variation of CT and LF excited-state energies, and both factors must be considered. The effect of CT perturbations can be treated by considering the reactant and product wave functions to be mixed through electron exchange coupling in the transition state. This model requires consideration of product (P) as well as reactant (R) electronic structure, and predicts a contribution to H_{PR} of the form

$$b \left(\frac{1}{E_{\text{CT}}^R} + \frac{1}{E_{\text{CT}}^P} \right)$$

from the lowest energy charge-transfer excited states of the reactants and products.

This approach provides a good correlation of observed retardation factors and excited-state electronic structures in Co(NH₃)₅X²⁺ reactions systems. Extension of the approach to other types of reaction systems, including some we reported earlier, is in progress.

Registry No. Co(sep)²⁺, 63218-22-4; Ru(NH₃)₆²⁺, 19052-44-9; Cr(bpy)₃²⁺, 17632-84-7; Co(NH₃)₆³⁺, 14695-95-5; Co(NH₃)₅cha³⁺, 102725-04-2; Co(NH₃)₅aniline³⁺, 91312-07-1; Co(NH₃)₅CN²⁺, 19529-81-8; Co(NH₃)₅Cl²⁺, 14970-14-0; Co(NH₃)₅Br²⁺, 14970-15-1; Co-

(NH₃)₅I²⁺, 15392-08-2; Co(NH₃)₅N₃²⁺, 14403-83-9; Co(NH₃)₅NO₂²⁺, 14482-68-9; *cis*-Co(en)₂(cha)Cl²⁺, 28121-20-2; *cis*-Co(en)₂(aniline)Cl²⁺, 46753-03-1; *cis*-Co(en)₂(benzylamine)Cl²⁺, 19306-83-3; *cis*-Co(en)₂(CN)Cl⁺, 75364-94-2; *cis*-Co(phen)₂(CN)₂⁺, 22806-53-7; Co(phen)₃³⁺, 18581-79-8; Co([14]aneN₄)(NH₃)₂³⁺, 53176-75-3; Co(Me₄[14]tetraeneN₄)(NH₃)₂³⁺, 36452-45-6; Co([14]aneN₄)(OH)₂³⁺, 46750-08-7; Co(Me₄[14]aneN₄)(OH)₂³⁺, 36452-48-9; *meso*-Co(bzo₃[12]hexaeneN₃)₂³⁺, 47872-01-5; *rac*-Co(bzo₃[12]hexaeneN₃)₂³⁺, 47872-04-8; [Co(en)₂

(NH₃)₃cha]Cl₃, 93966-10-0.

Supplementary Material Available: Details of parameters used in calculations of perturbational effects, and the quality of fit of Co(NH₃)₅X²⁺-Co(sep)²⁺ reactions data to the correlation parameters (3 pages). Ordering information is given on any current masthead page.

Marcus Theory in Organic Chemistry. Mechanisms of Electron Transfer and Proton Transfer from Aromatics and Their Cation Radicals

C. J. Schlesener, C. Amatore,¹ and J. K. Kochi*[†]

Chemistry Department, University of Houston, University Park, Houston, Texas 77004

(Received: January 15, 1986; In Final Form: March 18, 1986)

Methylarenes (ArCH₃) undergo electron transfer to tris(1,10-phenanthroline)iron(III) complexes (FeL₃³⁺) to afford the metastable cation radical ArCH₃^{•+}. The rigorous analysis of the kinetics allows the second-order rate constant *k*₁ for electron transfer to be evaluated together with the rate constant *k*₂ for the subsequent proton transfer from the various cation radicals ArCH₃^{•+} to different pyridines. The energetics of electron detachment from these ArCH₃ in solution (*E*_{Ar}^o) and in the gas phase (*I*_p) are measured by a novel microvoltammetric technique and from their photoelectron spectra, respectively. The applicability of the Marcus theory in the correlation of the electron-transfer rates (log *k*₁) with the driving force for methylarene oxidation (*E*_{Ar}^o) and FeL₃³⁺ reduction (*E*_{Fe}^o) is established for the endergonic region, and the dichotomy between activation and diffusional contributions is discussed. The Marcus evaluation of the inner- and outer-sphere reorganization energies accords with theoretical and experimental models of the structure and solvation of ArCH₃^{•+}. The Marcus equation also provides a viable free energy relationship for proton transfer from the methylarene cation radicals to widely different pyridine bases. The driving force includes the acidity constants *pK*_a^A for the methylarene cation radical and *pK*_a^B for the pyridine conjugate acid pyH⁺, together with the work terms *w*_p and *w*_r. The evaluations of the work terms *w*_p and *w*_r with the aid of the Marcus equation are discussed in the context of the transition state for proton transfer. Marcus theory thus provides a unifying basis for electron transfer and proton transfer in a single chemical system.

Introduction

Mechanisms in organic chemistry remain in a rather rudimentary state of development insofar as any unifying theory exists to allow the prediction of reaction rates. Heretofore the quantitative means to examine organic reaction mechanisms have largely depended on the use of various types of linear free energy correlations such as the Hammett and Brønsted relationships which are limited by the necessity of employing empirical constants.^{2,3} This situation is understandable if one considers that most organic reactions involve inner-sphere processes in which the activated complex is highly constrained.⁴ A conceptually more straightforward situation is represented by outer-sphere reactions, of which electron transfer is the simplest form. The development of Marcus theory of outer-sphere electron transfer thus provides the theoretical basis to potentially consider this class of organic reaction mechanisms in a quantitative, predictive way.^{5,6} Unfortunately the thorough application of Marcus theory to organic systems has been limited.⁷ The problem arises largely from the experimental difficulty of evaluating the standard electrode potentials *E*^o of the usual diamagnetic organic compounds, owing to the metastability of the associated cation and anion radicals.

We believe that aromatic systems offer an excellent opportunity to apply Marcus theory to organic chemistry since electron detachment or accession generates aromatic cation and anion radicals of which a wide variety have been identified.⁸ For our purposes, the methylarenes ArCH₃ are useful electron donors because they are known to undergo oxidative substitution reactions via the arene cation radical formed by either chemical or electrochemical methods.⁹ In particular, these arenes are subject to oxidative

degradation of the methyl side chain, as in the industrially important cobalt-catalyzed conversion of *p*-xylene to terephthalic acid.¹⁰ The results of numerous chemical and electrochemical studies are compatible with the initial steps which can be outlined

(1) Present address: Laboratoire de Chimie, Ecole Normale Supérieure, Paris, 75231.

(2) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

(3) (a) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Kosower, E. M. *Physical Organic Chemistry*; Wiley: New York, 1968.

(4) See, e.g.: Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

(5) Marcus, R. J.; Zwolinski, B. J.; Eyring, H. *J. Phys. Chem.* **1954**, *58*, 432. Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966. *J. Chem. Phys.* **1957**, *26*, 867; **1965**, *43*, 679; *Discuss. Faraday Soc.* **1960**, *29*, 21.

(6) For reviews, see: (a) Sutin, N. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973, Vol. 2, p 611. (b) Reynold, W. L.; Lumry, R. W. *Mechanism of Electron Transfer*; Ronald Press: New York, 1965. (c) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

(7) See: (a) Pelizzetti, E.; Mentasti, E.; Praumauro, E. *Inorg. Chem.* **1978**, *17*, 1181. (b) Pelizzetti, E.; Mentasti, E.; Barni, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 623. (c) Ebersson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192. (d) Pelizzetti, E.; Mentasti, E.; Praumauro, E. *Ibid.* **1978**, 620. (e) Ng, F. T.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 3606. (f) Cecil, R.; Littler, J. S., *J. Chem. Soc. B* **1968**, 1420; **1970**, 626, 632. See also: Ebersson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 29.

(8) See, e.g.: (a) Kaiser, E. T.; Kevan, L. *Radical Ions*; Wiley: New York, 1968. (b) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (c) Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. *Can. J. Chem.* **1984**, *62*, 2552.

(9) For a review, see: (a) Yoshida, K. *Electrooxidation in Organic Chemistry*; Wiley: New York, 1984. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.

(10) Landau, R.; Saffer, A. *Chem. Eng. Prog.* **1968**, *64*, 20.

[†] Dedicated to Rudy Marcus for his seminal contributions to the understanding of reaction dynamics.